

PATENT ABSTRACTS OF JAPAN

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(54) ACTIVE MATERIAL FOR LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance capacity by constituting an active material of Li, Cu, P and O elements of the specific ratio.

SOLUTION: An active material is expressed by a chemical formula $(\text{LiCu}_{1-x}\text{PO}_4)$. Here, $(0 \leq x \leq 1)$ is realized. In this active material, a crystal system is an orthorhombic system in $(0.5 < x < 1)$, and a unit lattice constant of its crystal lattice is $(a=5.31 \pm 0.5, \text{ and } b=13.43 \pm 0.5 \text{ and } c=4.91 \pm 0.5)$ in an angstrom unit. Such an active material is manufactured by heating it in two stages at 450°C , then, at 800°C after pressurizing/molding them into a pellet shape under pressure of 400 kgf/cm^2 by mixing them in the stoichiometric ratio of Li_2CO_3 , CuO and $(\text{NH}_4)_2\text{HPO}_4$. A battery is composed of a positive electrode having this active material, an electrolyte and a negative electrode being Li, an Li alloy, Li_xSnO_2 , carbon and/or a graphite material. To put it concretely, a battery having high capacity such as 600 mAh/g is obtained.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[The technical field to which invention belongs] this invention relates to a lithium cell.

[Description of the Prior Art] Many small rechargeable batteries are used as objects for consumer electronic equipment, such as a computer, a camcorder, and a cellular phone, as an important thing as portable power supplies, such as lighting of a tool or a toy. Recently, it has a new interest in the "lithium ion" rechargeable battery which used the intercalation compound which carries out occlusion discharge of the lithium as a negative electrode which changes a lithium secondary battery to a metal lithium. However, in this cell, it is necessary to choose carefully the host substance of a positive electrode and a negative electrode. LiMeO_2 (Me: Co, nickel) [Mat. Res. Bull. 15 (1980) 783 of the layer structure, J. Appl. Phys

19(1980) 305] and a three-dimensions spinel type oxide, and LiMn_2O_4 [Mat. Res. Bull. 18 (1983) 461, Mat. Res. Bull. 19 (1984) 179] -- one half of the times of a charging time value -- a lithium -- receiving -- about 4 -- it has the discharge voltage of V and attention is attracted as a positive active material for lithium ion batteries Recently, it inquires just about the ability of the positive-electrode matter of other kinds to use it for a lithium ion battery. These compounds are similar to Nasicon which consists of $\text{Li}_x\text{M}_2(\text{PO}_4)_3$ (M: Ti, V, Fe) and a three-dimensions skeletal structure like $\text{M}_2(\text{SO}_4)_3$ (M: Ti, Fe) [Solid State ionic 92(1996) 1]. In Japanese JP, 9, B -134725, 9-134724, and 9-171827, LiMPO_4 , M: nickel, and Co, Mn and Cu are indicated by the claim. The matter concerning this invention is a completely different kind, and these matter has olivine structure.

[Problem(s) to be Solved by the Invention] this invention aims at offering a new high capacity active material as an active material for lithium cells.

[Means for Solving the Problem] The active material for lithium cells which becomes this invention is characterized by what is expressed with chemical formula $\text{LiCu}_{1+x}\text{PO}_4$ ($0 \leq x \leq 1$). 2nd invention concerning the 1st invention is characterized by crystal system being orthorhombic system in $0.5 < x \leq 1$. 3rd invention concerning the 2nd invention is characterized by the unit-lattice constants of an orthorhombic-system crystal lattice being $a = 5.31 \times 0.5 \text{ \AA}$, $b = 13.43 \times 0.5 \text{ \AA}$, and $c = 4.91 \times 0.5 \text{ \AA}$. the thing concerning [the 4th invention concerning the 1st to 3rd invention] the manufacture method of the active material for lithium cells -- it is -- Li_2 -- it mixes by the stoichiometry-ratio of CO_3 , CuO , and $(\text{NH}_4)_2\text{HPO}_4$, pressurization molding is carried out by the pressure of 400 kgf/cm^2 at the shape of a pellet, and it is characterized by being 450 degrees C and subsequently heating two stages at 800 degrees C 5th invention is characterized by having an active material concerning the 1st, the 2nd, or 3rd invention about the positive electrode for lithium cells. 6th invention is characterized by consisting of negative electrodes which are the positive electrode concerning the 5th invention, the electrolytic solution and Li , Li alloy, Li_xSnO_2 , carbon, and/or graphite material about a cell.

[Embodiments of the Invention] Although this invention is explained in full detail based on the gestalt and drawing of 1 operation, it is not limited to this.

$\text{LiCu}_{1+x}\text{PO}_4$ ($0 \leq x \leq 0.5$) concerning a [example 1] this invention -- Li_2 -- it mixed by the stoichiometry-ratio of CO_3 , CuO , and $(\text{NH}_4)_2\text{HPO}_4$, and prepared by the single step reaction This

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mixture was mashed with the agate mortar, and it was made the pellet by the pressure of 400 kgf/cm², subsequently calcinated in 450-degree C heating air for 4 hours, and heated at 800 more degrees C for 24 hours. The obtained matter presented blue.

LiCu_{1+x}PO₄ (0.5 < X ≤ 1) concerning a [example 2] this invention -- Li₂ -- it mixed by the stoichiometry-ratio of CO₃, CuO, and (NH₄)₂HPO₄ **, and prepared by the single step reaction This mixture was mashed with the agate mortar, and it was made the pellet by the pressure of 400 kgf/cm², and subsequently it calcinated in 450-degree C heating air for 4 hours, and heated at 800 degrees C continuously for 24 hours. Consequently, the obtained matter presented green. A of drawing 1 and B show the X diffraction pattern in LiCu_{1+x}PO₄, X= 0, and X= 1 concerning this invention. The matter of X= 0 is difficult for there being many peaks and specifying a compound. Since this X diffraction pattern cannot be specified as mixture of the well-known compound containing Li, Cu, and phosphoric acid therefore, the author etc. has judged that it is that in which the matter of this invention has a new chemistry phase. The pattern with the same said of ** was observed by LiCu_{1+x}PO₄ of the range of 0 ≤ X ≤ 0.5. However, the X diffraction pattern of the matter of x= 1 can be specified by the orthorhombic-system symmetry, and unit-lattice constants are a= 5.31**0.5Å, b= 13.43**0.5Å, and c= 4.91**0.5Å. The same pattern was observed also in LiCu_{1+x}PO₄ of the range of 0.5 < X ≤ 1. Drawing 2 shows the cyclic BORUTAN meter of LiCuPO₄. This matter shows the single reduction peak to the 2.1V neighborhood without the corresponding oxidization peak. In this case, the trace speed was made into 0.2mV/min. and LiClO₄/2EC+2DMC+DEC was used as the electrolytic solution. Drawing 3 shows the cyclic BORUTAN meter of LiCu₂PO₄. This matter shows the single reduction peak without the corresponding oxidization peak near 1.8 VvsLi/Li+. And another another small reduction peak was observed near 1.2 VvsLi/Li+. In this case, the trace speed was made into 0.2mV/min. and LiClO₄/2EC+2DMC+DEC was used as the electrolytic solution. Drawing 4 shows the charge-and-discharge curve concerning the two cycle of the beginning of LiCuPO₄ which becomes this invention. This examination made current density 0.1 mA/cm², and was performed in the glass cell using LiClO₄/2EC+2DMC+DEC. This cell consists of a positive electrode (PVDF8% is included 87% [of active materials which become this invention], and carbon black 5%), and the lithium electrode and lithium reference electrode as a counter electrode. First, the cell was discharged and the lithium was inserted in the matter of this invention. This cell shows the flat potential of 2 VvsLi/Li+, and shows the high capacity of 600 mAh/g. The matter with many lithium contents was formed during electric discharge, and this large capacity is ***** (ed). Drawing 5 shows the X diffraction pattern of LiCuPO₄ after electric discharge. From this drawing, two new phases equivalent to Li₃PO₄ and metal Cooper were obtained. It is shown that LiCu_{1+x}PO₄ (0 ≤ X ≤ 1) decomposes this result into Li₃PO₄ and metal Cooper with many lithium contents in electric discharge process. Therefore, it is thought that the large service capacity observed by this matter is based on the generation of Li₃PO₄ with many lithium contents. Drawing 6 shows the Cu_{2p}XPS spectrum of LiCuPO₄ before and after electric discharge. A peak is shifted to the low 932.5eV binding energy side which shows metal Cooper's property after electric discharge. It checked that metal Cooper existed by this in LiCuPO₄ which discharged. [Effect of the Invention] About the new active material this invention is indicated to be by chemical formula LiCu_{1+x}PO₄ (0 ≤ X ≤ 1), this matter has the crystal structure which changed with X values, and its capacity is as high as 600 mAh/g, and it can use it as a positive active material of the lithium primary cell whose voltage is 2VvsLi/Li+.

[Translation done.]